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XPS monitoring of the removal of an aged polymer coating from a metal substrate by TEA-CO_2 laser ablation

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X-ray photoelectron spectrometry (XPS) has been used to observe the changes in surface chemistry during the removal of paint from a zinc coated steel substrate by means of TEA-CO_2 laser ablation. Laser ablation at both plasma and sub-plasma fluences is investigated and their relative merits are discussed. The laser is shown to be an effective tool for removal of the bulk of the paint layer and is not impaired by evidence of ageing in the paint. Evidence for a very thin layer of organic compounds present on the surface after cleaning at sub-plasma fluences has been found, although these can be removed at plasma fluences. © *1998 Kluwer Academic Publishers*

1. Introduction

Organic coatings (OCs), such as paints and lacquers, are widely used on a macroscopic scale as a form of protection for metals in buildings, vehicles [1] and monuments [2], and also on a much smaller scale, for example the insulation on copper wires [3]. These coatings provide a first line of defence against the corrosive influence of their environment and are subjected to aggressive conditions. The action of sunlight, temperature fluctuations and polluted rain-water can have severely deteriorating effects on most outdoor coatings over a period of only a few years after which they can be considered 'aged'. Ultra-violet radiation from sunlight can cause crosslinking and photo-oxidation of the polymer chains making them brittle and insoluble [2]. Physical effects, such as temperature fluctuations, induce stresses in the coating due to the differential expansion coefficients between the coating and the substrate, causing fracture and peeling [2, 4].

Removal of the aged coating, often by the use of solvents or abrasives, is normally required if it is to be replaced. The use of volatile solvents for aged coating removal is inefficient due to the effect of crosslinking decreasing their solubility; in addition, many countries have recently enforced restrictions on the use of volatile solvents due to environmental concerns. Abrasive methods also have environmental implications (e.g. sand-blasting in populated places) and they often damage the metal substrate. The shortfalls of these conventional cleaning methods have prompted research into alternatives including aqueous [5], CO_2 snow (micro-particle) [6], plasma [7], UV ozone [8], UV light [9] and UV laser cleaning [10] although all these processes have severe limitations in terms of efficiency and area processing capabilities.

The ability of C–C and C–O bonds to absorb 10.6 μm radiation from the CO_2 laser [11] makes all polymers absorptive of radiation in this region. Almost all metals, however, strongly reflect radiation of this wavelength. Thus, if high-powered, pulsed TEA-CO_2 laser radiation is focused onto the surface of a painted metal each pulse will vaporize or ablate a quantity of the polymer exposed to the beam. Once the polymer is removed and the metal substrate becomes exposed, the laser is reflected with negligible heating to the substrate. This 'self-limiting' process eliminates any danger of damage to the metal substrate. Excimer lasers (emitting ultra-violet radiation) have been used for ablation of organic polymers [12, 13] but do not exhibit as pronounced self-limiting characteristics if used on metal substrates due to the

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relatively high absorptivity of metals at ultraviolet wavelengths.

Excimer and Nd:YAG laser cleaning techniques have already found applications in many niche industries [14–16], including the removal of OCs from metals [3, 17], where damage to the substrate has to be avoided. The purpose of this paper is to explore the potential of TEA-CO_2 lasers for the removal of fresh and aged organic coatings from metals by using X-ray photoelectron spectrometry (XPS) to monitor the removal of a fresh and an aged polymer coating from a zinc-coated steel substrate.

2. Experimental

2.1. Materials

For our investigation, we needed both aged and fresh samples of the same coated metal. Accelerated ageing techniques for organic coatings using intense ultraviolet lights produce unpredictable results with questionable relevance to long-term exposure tests [18]. Long-term exposure tests require too much time for significant deterioration to take place.

A novel solution to this problem was applied by taking samples from the body panels of an old, dilapidated car. The zinc-coated steel bodywork was painted on both sides during manufacture such that the external side (ES) became exposed to weathering whilst the internal side (IS) was kept protected and effectively 'fresh'. The difference between the two sides was immediately apparent, the original gloss maintained by the IS had been lost by the ES. The number plate indicated the age of the vehicle to be 10 y. This method of obtaining samples left us without information as to the precise chemical nature of the samples (this was not freely available from the manufacturer), although elemental analysis would be provided by the XPS technique.

The samples were cut into 1 cm^2 squares for laser treatment and XPS analysis. The thickness of the ES and IS coatings were measured using a micrometer to be 13 and 8 μm respectively, the difference was to be expected due to the added protection the ES required from the more aggressive environment. Various off-white intermediate coatings were present between the maroon top-coat and the zinc-coated steel substrate. All the samples were cleaned with distilled water to remove surface contamination prior to any other treatment or analysis.

2.2. Laser cleaning

Cleaning was performed using a Laserbrand L450 TEA-CO_2 laser, emitting 10.6 μm radiation in a 100 ns pulse. All cleaning was performed at a fluence of about 2 $J\,cm^{-2}$ (insufficient to cause air-breakdown or 'plasma') except in the final tests, when cleaning with a plasma fluence was investigated using a fluence of about 8 $J\,cm^{-2}$ (just exceeding the plasma threshold).

Cleaning effects were of most interest in the region of the top-coat, where the effects of weathering could be found, and at the metal substrate, to detect any residues remaining after no further laser interaction was apparent. Thus, XPS measurements were made of both ES and IS samples at the following stages: on the original top-coat surfaces, before any laser cleaning was performed ('original'); after part of the top-coat had been removed by the laser ('partial laser'); after no further laser interaction took place and the metal substrate had become visible ('full laser'); and after laser treatment of the exposed metal substrate at plasma fluences ('plasma laser').

2.3. XPS measurements

XPS is a powerful technique in providing information about both the atomic composition of a surface (excluding H and He), and, at high resolution, the chemical environment of the different elements. The estimated depth of analysis is about 10 nm, which makes it particularly well suited for following surface chemical changes during the laser ablation process.

XPS experiments were carried out with a VG ESCALAB Mk 1 using AlK_α X-rays of energy 1486.6 eV, at a residual pressure of 1.3×10^{-5} Pa. Measurements were made using fixed analyser transmission and with the analyser normal to the plane of the sample surface at pass energies of 100 eV for broad scan spectra and 25 eV for high resolution scans of C1s, O1s and N1s peaks. Surface compositions were calculated using the areas of the respective photoelectron peaks after subtraction of a Shirley-type background. Correction has been made for the angular asymmetry of photoemissions [19], transmission of the energy analyser [20], photoionization cross-section [21] and the inelastic free path of the electrons [22]. The photoelectron peak broadening due to the X-ray line shape [23, 24] has been removed from the high resolution spectra using in-house software. Three spectra, each of three one-minute scans, were taken for each sample and the results averaged. High resolution spectra are accumulations of twenty scans.

Calibration of the high resolution peak positions has been made by using the main C–C/C–H component in the C1s spectra at 285 eV. An exception was made for the 'full laser' sample, where charge-induced broadenings and shifts were strong (see below) and the shape of the C1s peak was unreliable, so no attempt to assign position was made for this sample. All peak assignations have been made after Beamson and Briggs' database [25].

3. Results and discussion

3.1. Original surfaces

Table I shows the surface compositions measured for the different samples. The original top-coat paint layer presents a C/O based composition, typical of organic coatings; the added presence of N most likely forms part of the chromophere species providing the maroon colour; the Si component may come from polysiloxanes often added as surfactants, silicone wax polish, or both. Both Si and O atomic percentages are significantly higher in the outer side than in the inner one; environmental effects acting preferentially on the

TABLE I Atomic composition of the different samples.

Sample	Treatment	C (at %)	O (at %)	N (at %)	Si (at %)	P (at %)	Zn (at %)	Sn (at %)
ES	Original	65.6	24.2	6.8	3.5	–	–	–
	Partial laser	78.8	19.1	1.6	0.5	–	–	–
	Full laser	59.4	25.9	2.4	–	8.1	3.0	1.2
	Plasma laser	8.4	53.8	–	–	19.4	9.3	9.1
IS	Original	75.6	18.2	5.8	0.5	–	–	–
	Partial laser	78.5	19.7	1.5	0.2	–	–	–
	Full laser	62.2	23.9	2.7	–	8.3	2.1	0.8

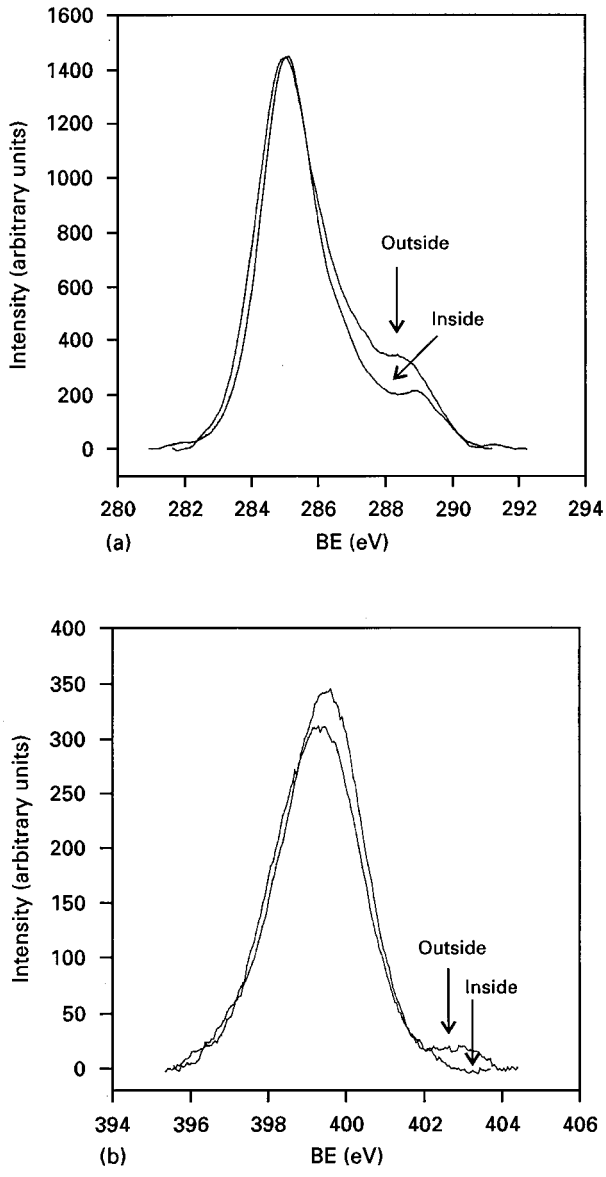

Figure 1 (a) C 1s and (b) N 1s high-resolution XPS spectra of the original ES and IS samples.

outer side, such as mild oxidation, would account for the excess O.

Evidence of weathering implied by the loss of gloss from the OS is confirmed and characterized by the XPS spectra. Oxidation is clear from the high resolution spectra of these samples. Fig. 1a and b show the C1s and N1s spectra of the original top-coat samples respectively. In Fig. 1a, C1s spectra of polymers present a peak at 285 eV corresponding to C/C and C/H bonds, and often smaller peaks at higher bonding energies corresponding to C/heteroatom bonds, their shift with respect to the main peak being more pronounced the more electronegative the heteroatom or the higher the bonding order. Therefore, given the chemical composition measured for these samples, there is a greater abundance of functionalities such as C–N, C=N, C–O, C=O O–C C=O, or even C single-bonded to three O, in the OS than in the IS. In Fig. 1b, the N1s OS spectrum presents an additional peak at around 403 eV, a position ascribable to N/O bonds and further evidence of weathering. The O1s spectra present a fairly symmetrical peak at around 532.9 eV, ascribable mainly to C–O, and no significant difference was observed between the OS and IS samples. Changes are expected to be more visible in the C1s and N1s spectra than in the O1s itself, where the relative changes are smaller.

3.2. Partial laser ablation

Compared to the original surfaces, the partial-laser top-coat compositions reveal a decrease in Si, probably brought about by ablation of a Si wax layer: and also a decrease in N which was accompanied by an observed fade in colour (although this fading can also have a physical origin due to an increased roughness of the ablated surface). Fig. 2 shows a decreased intensity in the intermediate shifts zone of the C1s peak, which proves the removal of mildly oxidized species originated by ambient exposure. As a result of this, a peak with a 4 eV shift with respect to the main peak is now better resolved which corresponds to carboxylic or polyester groups, both typical in paint formulations.

Comparing the OS and IS top-coat samples after the single laser shot (i.e. 'partial laser'), the compositions are virtually identical, as are the C1s spectra (see Fig. 2). Hence, all evidence of ageing is removed by a single laser pulse.

From our experience, the behaviour of metals and OCs under the effects of high power TEA-CO_2 laser pulses can be generalized to include most coated metal systems. OCs are significantly absorptive of 10.6 μm radiation due to the presence of C–C and C–O bonds [11, 26]. The effect of weathering can have a pronounced effect on the absorption spectra of OCs in the ultraviolet and visible regions (yellowing, for example), whilst the infrared region remains virtually

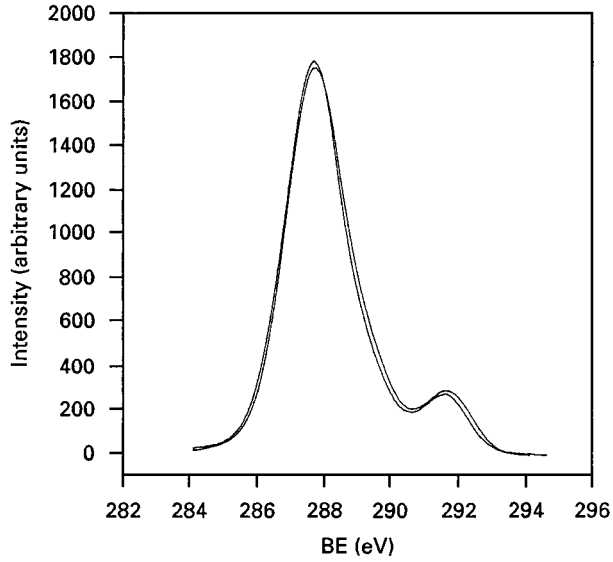

Figure 2 C 1s high-resolution XPS spectra of the 'partial laser' ES and IS samples.

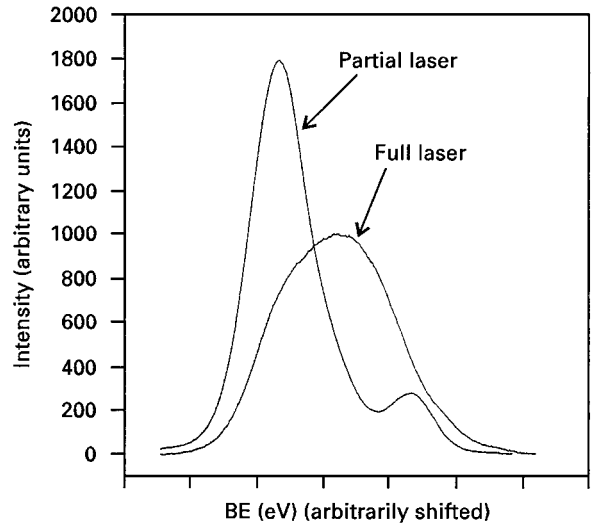

Figure 3 C 1s high resolution XPS spectra of the 'partial laser' and 'full laser' IS samples.

unaffected [2]. Pure metals and alloys have reflectivities that typically exceed 90% at 10.6 μm [27]. It should be noted, however, that this can be reduced significantly by the presence of oxides or other forms of contamination on the surface. Although no quantitative analysis was performed, the effect of weathering on the boiling point and thermal conductivity of the OCs did not appear to impair the efficiency of the cleaning process.

3.3. Full laser ablation and plasma-cleaning

The full-laser samples appear as tarnished metal and, to the naked eye, it appears that all of the paint has been removed. XPS of these samples reveal phosphorus and some Sn and Zn, both on the outer and inner surfaces (although both Sn and Zn are slightly higher on the outside). No iron was detected, which can be expected by the presence of a Zn coating on the steel (typically applied to a thickness of a few micrometres). This is a long recognized form of cathodic protection for steel, the Zn being applied by galvanizing, electroplating or spraying. As well as protecting the steel, Zn responds well to phosphate coating (the source of the observed P) which serves both as protection and improves adhesion between the coating and the substrate [28]. During manufacture, part of the zinc phosphate coating may be converted into stannous phosphate by dipping in a stannous chloride solution: this process further improves the coatings corrosion resistance [29] and accounts for the high levels of tin found near the surface of the zinc.

Other, non-metallic elements have also been detected on the full-laser samples; a large amount of O, most likely from the phosphate coating; some N is observed of unknown origin: but the most striking fact is that 60% C remains on the surface.

At first sight, the most obvious explanation for the high percentage of C remaining at the surface is that a thin, resilient paint layer remains after cleaning which, due to its proximity to a metal heat-sink, is not sufficiently heated by the laser to be removed. Such a phenomena has been observed by Brannon *et al.* [3] whilst using TEA-CO_2 lasers to strip polyurethane coatings from wires. Closer examination, however, using high resolution spectra as shown in Fig. 3, shows us that the remaining carbon peak has a very different appearance to that of the carbon in the original paint layer. The carbon in the original paint layer has two discernible peaks, the most significant for the C/C and C/H bonds and a smaller peak for the C/heteroatom bonds that are the required functional groups for paint formulations. This second peak, and therefore the functional groups seems to be absent in the remaining carbon layer which would imply that it is either a simple hydrocarbon or elemental carbon, but not paint. A more detailed analysis of this peak is prevented by strong charge-induced broadening and shifting effects. This difficulty in recording spectra of thin polymer films deposited on insulating substrates has also been recognised by other authors [30, 31]. At present we are uncertain as to the origins of this layer although possible explanations could be the redeposition of ablation products or some form of modification of the paint layer.

Alternatively, if the samples are cleaned at plasma fluence, the C diminishes to about 10% and is probably due to atmospheric contamination [32] prior to XPS examination. This effect has been confirmed by the zero contact-angle observed immediately after plasma cleaning which shows that all organics have been removed. Plasma cleaning causes all O, P, Sn and Zn to increase; P and O increase proportionally (both double), again supporting the idea that the oxygen is associated to the phosphorus and not to the carbon.

The formation of a plasma produces considerable amounts of UV radiation that could facilitate removal of the residual layer by photochemical (e.g. photodecomposition) mechanisms. However, in using a plasma to remove the residual layers the self-limiting nature of the process is sacrificed and significant

heating and subsequent oxidation of the metal substrate may result. It should also be noted that the plasma is opaque to the laser radiation and forms within the first quarter of the pulse, preventing the remainder of the beam from coupling with the surface. Thus, cleaning at a plasma fluence is more inefficient for removal of the bulk of the paint layer.

The practical implications of a residual layer remaining after cleaning could limit the use of lasers in certain applications where atomically clean surfaces are required.

4. Conclusions

The effect of weathering does not prevent the OC being removed by the laser and should not affect the ability of the laser to remove OCs in general. TEA-CO_2 lasers have the potential to be used in, for example, the removal of aged paints and lacquers during the restoration of statues [2].

At sub-plasma fluences, the laser selectively removes the bulk of the organic coating, leaving inorganic (metallic element and covalent oxide) compounds and a thin organic layer.

At plasma fluences, the laser can remove any remnants left from sub-plasma cleaning, but may induce significant heating of the metal substrate.

The general absorption characteristics of metals and OCs in the far infrared should facilitate the reliable extrapolation of results to other metal/OC systems.

Even for thick coatings such as these (of the order of 10 μm), cleaning rates of 1 $cm^2 s^{-1}$ are achievable with the present system operating at 10 Hz.

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